ESTIMATION OF THE DRY DEPOSITION VELOCITY AND SCAVENGING RATIO FOR ORGANIC CHEMICALS

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INTRODUCTION

Some case studies of the deposition of organics have been well documented, e.g., the deposition of PCB's in the Great Lakes (Murphy and Reszutko, 1978; Eisenreich, et al., 1981); however, the quantification of the deposition of organics is generally very sparse. The variety of toxic organic compounds, coupled with the relative lack of physicochemical property data and ambient concentrations, further hampers our ability to address their deposition, and the water quality problems which may ensue from their atmospheric release. It is infeasible to evaluate the deposition properties of each of these chemicals to the extent that we have studied the deposition of heavy metals, or sulfur oxides. Thus, it will be useful to develop methods for estimating the deposition properties of organic chemicals based on their physicochemical properties. In the extreme, it may be necessary to base these estimates on chemical structure alone. This paper is a rudimentary step in the development of such methods. The method presented is a crude one, which nonetheless exhibits order-of-magnitude accuracy in estimating deposition velocity and precipitation scavenging ratio for a range of organic compounds.

The method may be appropriately labeled as a screening method -- more accurate and detailed characterizations of some of the phenomena considered are certainly feasible based on the state-of-the-art. However, more detailed analysis may not always be appropriate, based on considerations of data availability, seriousness of the environmental concern and level of resources which may be committed to routine evaluation of many compounds. A screening method, such as the one presented below, permits rapid evaluation of numerous compounds, focussing attention on particularly problematical ones for more detailed analysis.

We address only the climatological mean deposition properties, using characteristics of the atmospheric boundary layer which represent "typical" conditions over the continental U.S. Deposition of many trace organics is controlled by the interfacial resistance rather than resistance of the turbulent boundary layers, thereby muting the effect of meteorological controls. Finally, the exposure scenarios of concern for many trace organics are of a chronic, long-term

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nature, implying that short term fluctuations in concentration and exchange rate are relatively unimportant. The methods should not be blindly applied to studies of acute exposure from chemical spills.

PHYSICAL/CHEMICAL PHENOMENA CONTROLLING DEPOSITION OF ORGANICS

The development of predictive equations for the relationships between physicochemical properties and the deposition parameters is presented in detail by Tucker and Preston (in press) and will only be summarized here.

The Airborne Reservoir of Organic Compounds: Vapor and Aerosol Phases. The airborne reservoir of an organic compound generally consists of both a vapor and aerosol phase. In many practical circumstances, the aerosol phase consists predominantly of contaminant adsorbed to the surfaces of ambient aerosols in quasi-equilibrium with the vapor phase. At equilibrium the fraction of the airborne reservoir which exists as an aerosol, ϕ, is principally dependent on the compound's saturation vapor pressure and the available aerosol surface area, as discussed by Junge (1977). In the broadest terms, the deposition rate of the vapor phase is dependent on the chemical properties of the contaminant and meteorological factors, while the deposition of the aerosol phase depends on the aerosol size distribution and meteorological factors (Sehmel and Hodgson, 1974; Gatz (1976). Methods for evaluating the effects of chemical properties on deposition parameters are not available, nor is there much known about the aerosol size distribution of the aerosol phase of trace organics. Given the partitioning between vapor and adsorbed phases, the deposition parameters for the total airborne contaminant mass may be represented by the mass weighted average of parameter values associated with the individual phases, i.e.,

$$W_d = W_{d,v}(1 - \phi) + W_{d,s}(\phi) \tag{1}$$

$$r = r_v(1 - \phi) + r_s(\phi) \tag{2}$$

Aerosol Size Distribution of Surface Adsorbed Contaminant. The mass of organic compound adsorbed to aerosol surfaces is dependent on the available aerosol surface area, Junge (1977). A reasonable extension or corollary to his findings is that the same is true for specific aerosol size fractions, i.e., if 20% of the ambient aerosol surface area is associated with particles of diameter 0.5 μm to 1.0 μm, then 20% of the adsorbed contaminant will be associated with particles in that size range. This assumption is expected to be true to first order. Second order complications are discussed by Tucker and Preston (in press). This assumption leads to the hypothesis that the mass median diameter of the adsorbed fraction of a trace organic compound in equilibrium with its vapor phase is approximated by the surface area median diameter (d_a^{50}, the diameter for which

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The surface area median diameter, d_a^{50}, of natural aerosols is typically 0.1 μm or less; for wind-blown dusts from disturbed agricultural lands may approach 0.5 μm; and from the outlet of an electrostatic precipitator from a coal fired power plant is approximately 0.2 μm. Thus, the mass median diameter of adsorbed trace organics is generally expected to be much less than 1 μm. Uncontrolled fly ash from coal combustion exhibits a surface area median diameter of 1-3 μm. Based on these d_a^{50} values, the hypothesis is supported by observations by Doskey & Andren (1980) and Van Vaeck & Van Cauwenberghe (1978) for PCB's and PAH's, respectively.

Dry Deposition of the Vapor Phase of Trace Organics. Dry deposition rates for both gases and aerosols have been shown to depend on the physical and chemical properties of the deposition surface. However, the variations associated with different surfaces are usually less than an order of magnitude (see, for example, Scott et al., 1981, and Peterson, 1977). Likewise variations associated with meteorological conditions are generally recognized to result in short-term variations in deposition velocity of one to two orders of magnitude. On the other hand, over long averaging times, the deposition characteristics of different sites in the continental U.S. are unlikely to differ by as much as an order of magnitude as a result of meteorological differences between the sites. Variations in the deposition velocities of different compounds, however, may differ by several orders of magnitude as a result of differences in the chemical properties of the compounds. For example, Bidleman and Christensen (1979) observed that the average dry deposition velocities of a very limited set of high molecular weight chlorinated hydrocarbons range over a factor of 30. In this same study, the differences in average dry deposition velocities of specific compounds at two different sites were about a factor of 3-4. Thus, the emphasis on meteorological and surface factors evident in the deposition literature, is not appropriate for the development of general methods to estimate the deposition velocity of organic compounds.

In an attempt to deduce the effect of compound-specific physical-chemical properties on deposition velocity, a semiempirical approach has been adopted. Theoretical considerations have been accounted for in identifying the controlling chemical properties and the general form in which the properties are expected to relate to the dry deposition velocity. Then an empirical regression analysis is used to determine the most successful formula for predicting dry deposition of vapors. Probably the most important assumption made in the theoretical

development is that the dominant chemical reaction between the airborne contaminant and the surface is the interaction with surface water. For chemicals which do not satisfy this condition, the method may be inaccurate. Although adoption of this assumption limits the technical validity of the method to air-water exchange, as a practical matter the method will also be suitable for the deposition of many chemicals to land surfaces based on several considerations detailed by Tucker and Preston (in press).

The result of theoretical analysis of air-water exchange of organic vapors is that the parameter, D, where

$$D = \left[\frac{.0225}{D_a} + \frac{H}{23.8\ D_w + .042\ k_w} \right] \tag{3}$$

should be inversely proportional to dry deposition velocity. The dry deposition velocity of 15 gases available in the literature (Peterson, 1977) was significantly correlated with $W_{d,v}$ (r = .78) so empirical analysis was used to improve the predictive power of the formula. The 15 gases include both organic and inorganic vapors, all highly volatile such that aerosol deposition is not a factor in the observed deposition velocity. Regression analysis indicated that the following formula provided the best fit between these parameters:

$$\log V_{d,v} = -.383 \log \left[\frac{.0225}{D_a} + \frac{H}{23.8\ D_w + .042 k_w} \right] + .576 \tag{4}$$

The accuracy is still quite limited. The standard deviation of the residuals about $\log V_d$ is 0.65, implying that predictions are only good with 90% confidence to within a factor of 12. For cases in which the dry deposition of gaseous pollutant is the primary removal mechanism, this level of uncertainty will also apply to the overall deposition velocity. However, if $W_{d,v}(1-\phi) \ll W_{d,s}(\phi)$, then uncertainty in $W_{d,v}$ will be inconsequential. Note that the equation implies that the reaction rate is insignificant if $k_w < 500\ D_w$.

Dry Deposition Velocity Estimation for the Sorbed Contaminant. For the fraction of airborne contaminant which is adsorbed, the dry deposition velocity, $W_{d,s}$ is solely a function of particle size, meteorological conditions, and surface conditions. The effects of such factors have been investigated extensively by several investigators, most notably Sehmel & Hodgson (1974), and will not be further elaborated here. In pursuit of a simple screening method, applicable over a typical climatological ensemble of meteorological conditions, a wide range of surface types, for adsorbed contaminants associated with a wide range of particle sizes (mass median diameters of .1 to 3 μm), the available data is not inconsistent with a rule-of-thumb that $W_{d,s} \approx 0.5 - 1$ cm/sec. More

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sophisticated and precise analysis is certainly feasible, and would be warranted if "order-of-magnitude" precision is deemed insufficient. However, at the current state-of-the-art in estimation of deposition properties of organic compounds it is difficult to justify more detailed analyses for a routine chemical by chemical assessment of deposition phenomena.

Wet Deposition. The simplest technique for estimating wet deposition rate, or rainfall contaminant concentration, is the washout or scavenging ratio approach. The scavenging ratio, r, is defined as the ratio of rainfall concentration to air concentration at ground level. The scavenging ratio is expected to be a constant for equilibrium scavenging of vapors, or if the rainfall contaminant loading results principally from near surface washout of aerosols. Nonetheless, Gatz (1976) has observed relatively constant scavenging ratios for several heavy metals (reflecting a particle size dependence) under a wide range of meteorological situations and source configurations suggesting a widespread practical applicability of this approach.

The washout ratios for particulates, r_s, have been shown by Gatz (1976) and others to be a function of particle size. The appropriate size distribution for the adsorbed contaminant is estimated as in Section 2b. The scavenging ratio for gases is approximated adequately by the inverse of the Henry's Law Constant, H. Note that at high vapor pressures (when $\phi << 10^{-3}$), $r \approx r_v$.

ESTIMATION OF CHEMICAL PROPERTIES

Each of the physical chemical properties identified as controlling the deposition parameters in the foregoing section may be estimated from other fundamental properties, or in the extreme case, from molecular structure alone. Methods for estimating these properties have been thoroughly reviewed and summarized in a recent book by Lyman et al. (1982). In any actual application of the methods presented here one would, of course, rely on the best available data. However, as an extreme test of this theory we present herein estimates based on structure alone, regardless of the availability of measured property data.

Vapor Pressure. This section describes how the vapor pressures of complex organic molecules can, when necessary, be roughly estimated from structural information alone. For the twelve study compounds, the only approach available is a two-step procedure involving first the estimation of a boiling point (T_b) and second the use of this boiling point to estimate a vapor pressure (P_{vp}). (It does not matter that a compound may not have a real boiling point due to decomposition at a lower temperature.) This approach has two serious problems. First, the available structure-based estimation methods for the boiling point

have never been adequately tested for large, multifunctional, multiring molecules; estimation method errors are likely to be 5-10% (for T_b in K) at best. Second, the estimation of P_{vp} from T_b is, essentially, an extrapolation from one vapor pressure (760 mm Hg at the normal boiling point) to another. When this extrapolation must cover, as in our case, five to ten orders of magnitude, significant errors can be involved. Propagated error, due to the uncertainty in T_b, will also be large because of the nearly exponential relationship between P_{vp} and T_b.

When experimental boiling points are used to estimate vapor pressures, values of P_{vp} as low as 10^{-5} mm Hg can often be obtained with $\pm$ 40-60% of the correct value. The use of estimated boiling points, and the extrapolation to lower values of P_{vp}, will usually result in estimation method errors of one to two orders of magnitude, at least.

Structure-based estimation methods for T_b are described in many works including Gold and Ogle (1969), Reid and Sherwood (1966), Cramer (1980) and Rechsteiner (1982). Three methods were chosen for trial in this study: (1) Meisner; (2) Lydersen-Forman-Thodos; and (3) Miller. (All of these are described by Rechsteiner (1982). The estimated boiling points using the three selected methods are shown in Table 1; measured values are also shown, if available.

The estimated boiling points were used to estimate vapor pressures (at 25°C) using a method described by Grain (1982). The estimated values of P_{vp} are shown in Table 2 along with measured values if available. An inspection of the quality of predictions shown in Tables 1 and 2 leads us to conclude that the approach using Method 1 for boiling points provides the more reliable set of estimates. Method errors in the estimation of P_{vp} by this route (Method 1 for T_b) do appear to be in the range of one to two orders of magnitude. Such estimates should be sufficient for preliminary environmental assessments.

Diffusion Coefficients. Molecular diffusion coefficients in air, D_a, may be estimated adequately for nonpolar organic gases as described by Tucker & Nelken (1982). The method has been demonstrated to have an absolute average error of 7.6% for a test set of 128 gases. The estimated values of D_a are presented for five compounds for which dry deposition observation are available (see Section 4) in Table 3.

Molecular diffusion coefficients in water, D_a, have been estimated as described by Tucker & Nelken (1982). The average absolute error compiled in a test on 87 solutes was 5.8%. The estimated values of D_a are presented for the same five compounds in Table 3.

Henry's Law Constant. When necessary, Henry's law constant (H) can be estimated directly from structural information alone. (Whenever possible, however,

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TABLE 1

BOILING POINTS FOR STUDY COMPOUNDS (All Values in Kelvin)

Compound	Reference Values	Estimated From Structure[a]		
		Method 1	Method 2	Method 3
Aroclor 1016	mid pt. 614[b]	591	609	557
Aroclor 1242	mid pt. 619[b]	591	509	557
Aroclor 1254	mid pt. 651[b]	626	683	586
Chlordane		638	636	535
Dieldrin		625	677	538
Toxaphene		633	624	519
p,p´-DDT		642	1697(?)[d]	588
p,p´-DDE		623	896(?)[d]	549
Hexachlorocyclohexane	[α] 561[c] [γ] 597[c] [β] 617[c] [δ] 613[c]	526	576	509
Hexochlorobenzene	subl. 595[c]	527	556	515
Di-n-butylphthalate	613[b]	585	1010(?)[d]	806
Di(2-ethylhexyl) phthalate		696	848(?)[d]	724

[a]Method 1: Meissner; Method 2: Lydersen-Forman-Thodos; Method 3: Miller (see text for references). [b]Weast (1970). [c]Callahan et al. (1979). [d]Application of estimation method unclear.

estimates based upon the ratio of vapor pressure (P_{vp}) to solubility (S) should be given preference if S < 1 mol/L.) Recent studies at A.D. Little, Inc., have led to a clear preference for the group method of Hine and Mookerjee (1975) over other structure-based methods that are available (e.g., Cramer, 1980). Estimation method errors for H appear to average about 0.1 log units (~25%) for hydrocarbons and monofunctional compounds, and about 1.1 log units (~ factor of 10) for compounds with two or more functional groups. The other methods are not only less accurate, but more difficult to employ.

Our estimates of H using the method of Hine and Mookerjee (1975) are shown in Table 4 along with reference values. It was necessary, as in the estimation of boiling points, to assume a particular structure for the Aroclors and Toxaphene.

Reaction Rate in Water. We have not compiled the available data (or derived estimates) for reaction rates in water for the twelve study chemicals since it is fairly clear that the reaction rates will be low enough not to be an important factor in the deposition process. In particular, it can be shown that reactivity will be relatively unimportant in the deposition process if the overall, first-

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TABLE 2

VAPOR PRESSURES FOR STUDY COMPOUNDS (Units are mm Hg; T ≈ 25°C)

Compound	Reference Values[a]	Estimated From Structure[b]		
		Method 1	Method 2	Method 3
Aroclor 1016	4.0×10^{-4}	2.9×10^{-3}	1.3×10^{-3}	1.4×10^{-2}
Aroclor 1242	1.3×10^{-3}	2.9×10^{-3}	1.3×10^{-3}	1.4×10^{-2}
Aroclor 1254	7.7×10^{-5}	5.8×10^{-4}	4.1×10^{-5}	3.6×10^{-3}
Chlordane	1.0×10^{-5}	9.7×10^{-8}	1.2×10^{-7}	1.7×10^{-3}
Dieldrin	1.8×10^{-7}	3.9×10^{-7}	3.5×10^{-9}	1.6×10^{-3}
Toxaphene	1×10^{-6} [c, i] 3×10^{-7} [d, j]	1.5×10^{-7}	3.4×10^{-7}	5.0×10^{-3}
p,p´-DDT	3.1×10^{-6} 2.0×10^{-7} [c]	8.5×10^{-8}	$(<10^{-20})$	5.4×10^{-5}
p,p´-DDT	6.4×10^{-6} 1.3×10^{-5} [f, i] 1.4×10^{-5} [g, i]	4.6×10^{-7}	1.4×10^{-9}	7.7×10^{-4}
Hexachlorocyclohexane	[α] 2.5×10^{-5} [γ] 1.6×10^{-4} [γ] 6.3×10^{-5} [b] [ß] 2.8×10^{-7} [δ] 1.7×10^{-5}	2.5×10^{-3}	7.9×10^{-5}	7.5×10^{-3}
Hexachlorobenzene	1.1×10^{-5}	3.3×10^{-3}	4.9×10^{-4}	7.5×10^{-3}
Di-n-butylphthalate	1.6×10^{-4}	3.8×10^{-3}	4.6×10^{-12}	1.1×10^{-7}
Di-(2-ethylhexyl)phthalate	2.0×10^{-7}	2.2×10^{-5}	1.4×10^{-8}	5.6×10^{-6}

[a]SRI (1980) unless otherwise noted. [b]Estimated by method of Grain (1982) with boiling points as follows: Method 1: Meisner; Method 2: Lyderson-Forman-Thodos; Method 3: Miller. [c]Seiber et al. (1981). [d]Spencer (1973). [e]Neely (1982). [f]Westcott et al. (1981). [g]Westcott and Bidleman (1981). [h]Mackay and Shiu (1981). [i]At 30°C. [j]At 20°C.

TABLE 3

ESTIMATED MOLECULAR DIFFUSION COEFFICIENTS OF STUDY COMPOUNDS

	In water, D_w cm^2/sec	In air, D_a cm^2/sec
Arochlor 1016	5.9×10^{-6}	5×10^{-2}
Arochlor 1254	5.4×10^{-6}	4.9×10^{-2}
Chlordane	4.9×10^{-6}	4.5×10^{-2}
p´p´-DDT	4.9×10^{-6}	4.6×10^{-2}
Toxaphene	4.7×10^{-6}	4.4×10^{-2}

TABLE 4

HENRY'S LAW

Compound

Aroclor 10

Aroclor 12

Aroclor 12

Chlordane

Dieldrin

Toxaphene

p,p´-DDT

p,p´-DDE

Hexachlor

Hexachlor

Di-n-buty

Di(2-ethy

[a]Values ma ratio. [b] [d]Levins (1 [g]Warner et

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om Structure[b]	
d 2	Method 3
0^{-3}	1.4×10^{-2}
0^{-3}	1.4×10^{-2}
0^{-5}	3.6×10^{-3}
0^{-7}	1.7×10^{-3}
0^{-9}	1.6×10^{-3}
0^{-7}	5.0×10^{-3}
$20)$	5.4×10^{-5}
-9	7.7×10^{-4}
-5	7.5×10^{-3}
-4	7.5×10^{-3}
-12	1.1×10^{-7}
8	5.6×10^{-6}

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TABLE 4

HENRY'S LAW CONSTANT FOR STUDY COMPOUNDS (Units are $atm \cdot m^3/mol$; $T \simeq 25°C$)

Compound		Reference Values[a]	Estimated from Structure[b]
Aroclor 1016		1.4×10^{-2} c	4.7×10^{-5}
		*3.2×10^{-4} d	
		2.7×10^{-6} e	
Aroclor 1242		7.6×10^{-3} c	4.7×10^{-5}
		*5.7×10^{-4} f	
		*2.0×10^{-3} d	
Aroclor 1254		8.4×10^{-3} g	3.4×10^{-5}
		*2.8×10^{-3} f	
		*1.1×10^{-3} d	
Chlordane		4.8×10^{-5} g	3.4×10^{-5}
		*2.9×10^{-6} d	
Dieldrin		5.8×10^{-5} g	1.7×10^{-6}
		*1.1×10^{-5} h	
		*4.5×10^{-7} d	
Toxaphene		4.9×10^{-3} g	4.5×10^{-4}
p,p´-DDT		*5.2×10^{-5} h	4.6×10^{-6}
		*7.2×10^{-5} d	
p,p´-DDE		*2.7×10^{-4} d	7.7×10^{-6}
Hexachlorobenzene		1.7×10^{-3} g	2.0×10^{-3}
		*4.9×10^{-5} h	
Hexachlorocyclohexane	[γ]	*3.2×10^{-6} h	4.2×10^{-11}
	[α]	*6.0×10^{-6} d	
	[γ]	*8.2×10^{-6} d	
	[β]	*4.5×10^{-7} d	
	[δ]	*2.1×10^{-7} d	
Di-n-butylphthalate		*4.5×10^{-6} d	4.4×10^{-7}
Di(2-ethylhexyl)phthalate		*2.6×10^{-7} d	3.1×10^{-5}

[a]Values marked with asterisk are derived from the vapor pressure/solubility ratio. [b]Using group method of Hine and Mookerjee (1975). [c]Paris et al. (1978). [d]Levins (1981). [e]Doskey and Andren (1981). [f]Mackay and Leinonen (1975). [g]Warner et al. (1980). [h]Mackay and Shiu (1981).

order reaction rate, k_w (sec^{-1}), is much less than 500 D_w, where D_w (cm^2/sec) is the pollutant's diffusion coefficient in water. Since D_w will typically be $\leq 10^{-5}$ cm^2/sec, we must have $k_w \ll 5.7 \times 10^{-3}$ sec^{-1} or a half-life in the water of more than 2 minutes.

APPLICATION OF AIR-TO-SURFACE PATHWAY SCREENING AND COMPARISON WITH OBSERVATIONS

The foregoing relationships may be integrated into a predictive method. The method developed is similar in many respects to that presented by Scott et al. (1981) who also present further discussion of the physical processes leading to such relationships and their limitations in practice. The most significant difference between this approach and the recommendations of Eisenreich et al. (1981) and of Scott et al. (1981) are (1) the presentation here of a consistent framework for treating vapor and aerosol phases in both wet and dry deposition, and (2) the semiempirical expression (Eq. 4 for $V_{d,v}$ and (3) the ultimate reliance on estimation from chemical structure. Further, we believe that several distinct categories of source types exhibit predictable gross features of vapor/aerosol partitioning and aerosol size distribution which can lead to useful estimates of the deposition rate. Four different release modes are characterized by Tucker and Preston (in press). For the compounds studied here only Release Mode 1 (released as a vapor into ambient air) is appropriate. Vapor is assumed to equilibrate with ambient aerosol; the mass median diameter is approximated as 0.4 μm for persistent chemicals; 0.1 μm for those which are reactive in the atmosphere ($k > 2.6 \times 10^{-6}$ sec^{-1}).

Overall, the method presented here requires less specific and more easily attainable input parameters, and rests more critically on some crucial assumptions than the approach recommended by Eisenreich et al. (1981) and Scott et al. (1981). An exemplary success of the similar procedures recommended by Eisenreich et al. (1981), Scott et al. (1981), and this paper, is the quantification of PCB deposition to the Great Lakes, which is controlled by the sorbed fraction. The results of application of the methods presented in this paper are similar to the results obtained by Eisenreich et al. (1981) for PCB's and will not be examined here.

Applications of the method based on available data sources will be presented to demonstrate the ability of these procedures to estimate rainfall concentrations, and wet and dry deposition rates, within an order of magnitude - an accuracy useful for screening analysis. The examples include:

- estimation of scavenging ratios for chlorinated hydrocarbons at a "pristine" location
- estimation of the dry deposition velocity for several chlorinated hydrocarbons in the American eastern seaboard

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Estimation of Scavenging Ratio for Nine Toxic Organics in a Remote Locale

(Enewetak Atoll, North Pacific). Atlas and Giam (1981) reported air and rainfall concentrations for PCB Aroclor 1242, hexachlorobenzene, d-hexachloro-cyclohexane, x-hexachlorocyclohexane, Chlordane (d and y), Dieldrin, p,p´-DDE, Di-n-butyl phthalate and Di(y-ethylhexyl) phthalate. In this remote location, it is assumed that the organics have reached equilibrium with the ambient aerosol, regardless of their original mode of release. The ambient aerosol is assumed to fall within the range of "clean air" aerosols as characterized by Junge (1977) so $\theta \simeq 10^{-7}$ cm^2/cm^3. The appropriate mass median diameter is 0.4 μm. Estimated and observed concentrations in rain shown in Table 5, along, along with needed input parameters for estimation. For five of the contaminants, PCB Aroclor 1242, hexachlorobenzene, Chlordane, Dieldrin, and p,p´-DDE, the observations provide only an upper bound on the scavenging ratios.

The estimated rainfall concentrations are substantially in error for the hexa-chlorocyclohexanes, Chlordane, and Dieldrin. Tucker and Preston (in press) demonstrate substantially better skill in estimating scavenging ratios for this same data set when relying on experimental values of vapor pressure and Henry's Law constant. Thus, part of the blame for the poor estimates here must rest with the estimation techniques for Henry's Law constant (in the case of hexa-chlorocyclohexane) and vapor pressure (of Chlordane). The estimation methods for those properties have not been sufficiently developed for multiply halogenated compounds.

Estimation of Dry Deposition Velocity for Several Chlorinated Hydrocarbons.

Bidleman and Christensen (1979) observed the dry deposition velocity for Chlor-dane, Toxaphene, p,p´-DDT, and Arochlor 1254 at rural sites on the east coast of the United States. Observations were made encompassing all seasons in South Carolina, and a more limited set during the fall, winter and spring in Rhode Island. We have taken a flux-weighted average of all the observed values for comparison with the estimated values which are intended to represent the climato-logical average. Observed and estimated values are presented in Table 6. The correlation between observed and predicted values is 0.57, which is not signifi-cantly different from 0 for such a small sample size. All observations are within a factor of 10 of the estimated value.

The data base for testing the method for dry deposition velocity is not as extensive as that for scavenging ratios. Neither are the methods for observing dry deposition as straightforward or standardized as the methods for estimating scavenging ratios (simple collection and analysis of bulk air and water concen-trations). All in all, the test of the estimation method for dry deposition

TABLE 5

COMPARISON OF OBSERVED AND ESTIMATED RAINFALL CONCENTRATIONS FOR NINE
ORGANIC COMPOUNDS AT ENEWETAK ATOLL

	Estimated			Observed
	r_v	$\emptyset$	r	r
PCB Arochlor 1242	520	2.8×10^{-5}	520	< 1100
Hexachlorobenzene	12	2.5×10^{-5}	14	< 300
α - Hexachlorocyclohexane	5.8×10^8	3.3×10^{-5}	5.8×10^8	1.2×10^4
γ - Hexachlorocyclohexane	5.8×10^8	3.3×10^{-5}	5.8×10^8	3.4×10^4
Chlordane	720	0.25	1.3×10^4	$< 1.5 \times 10^3$
Dieldrin	1.4×10^4	0.29	2.8×10^4	$< 2 \times 10^3$
p,p´ - DDE	3200	0.09	7.4×10^3	$< 7 \times 10^3$
Di-n-butylphthalate	5.5×10^4	2.2×10^{-5}	5.5×10^4	3.6×104
Di(2-ethylhexyl)phthalate	790	0.27	1.7×10^4	3.9×10^4

TABLE 6

COMPARISON OF OBSERVED AND ESTIMATED DRY DEPOSITION VELOCITY
FOR FIVE ORGANIC CHEMICALS

Compound	Estimated $V_{d,v}$ (cm/sec)	Estimated Sorbed Fraction of Airborne Reservoir	Estimated V_d (cm/sec)	Observed V_d (cm/sec)
Chlordane	0.10	0.6	0.6	0.13
Toxaphene	0.035	0.5	0.5	.33
p,p'-DDT	0.21	0.6	0.7	5.2
Arochlor 1016	0.09	10^{-3}	0.09	0.08
Arochlor 1254	0.10	10^{-4}	0.10	0.59

velocity is promising, but far from conclusive. We note that there are no alter-
native methods which require as little data as the method presented here.

Discussion. The methods for estimating both dry deposition velocity and
scavenging ratio can be shown to be most sensitive to the vapor pressure as it
controls vapor/aerosol partitioning. The theoretical and experimental basis for
defining the relationship between partitioning and vapor pressure is spotty, so
that even if the vapor pressure is known precisely there is little basis for
confidence in an estimated partitioning coefficient, ϕ. The problems are com-
pounded further by relying on an estimated vapor pressure. For the highly
chlorinated chemicals studied here, the estimated vapor pressure were typically
off by a factor of 14, compromising our ability to estimate ϕ.

FOR NINE

Observed r
<1100
<300
1.2×10^4
3.4×10^4
$<1.5 \times 10^3$
$<2 \times 10^3$
$<7 \times 10^3$
3.6×104
3.9×10^4

d	Observed V_d (cm/sec)
	0.13
	.33
	2
	.08
	0.59

here are no alter-
nted here.
velocity and
pressure as it
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For compounds with high vapor pressures (say 10^{-4} or higher), the deposition parameter estimates will also be sensitive to the Henry's Law constants. Estimation methods are not well developed for the multiply halogenated compounds studied here, exhibiting a typical error of a factor of 29 from reference values.

For compounds with low vapor pressures the assumptions regarding deposition of the airborne fraction become important. The size distribution inferred from the Release Scenario, and the scavenging ratio and dry deposition velocity inferred for submicron aerosols are highly uncertain, but their influence on the estimates cannot be easily evaluated from these data.

The scavenging ratio inferred for submicron aerosols, from data published by Gatz (1976) was 6×10^4. Use of a lower value would improve the scavenging ratio estimates for Chlordane, Dieldrin and p,p´-DDE, degrade the estimation of Di(2-ehtyhexyl) phthalate and leave other compounds virtually unchanged.

The changes in estimates attendant to a change in the assumed dry deposition velocity of submicron aerosols from 1 to 0.5 cm/sec would be minor, slightly worsening the estimate for p,p´-DDT and leaving the Arochlors unchanged. Such fine tuning is not justified on the basis of these findings in light of other errors of greater magnitude probable in both the estimation methods and the observational data.

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DISCUSSION

R. D. DELUMYEA: The chemical properties of a molecular species (boiling point, dipole, reactivity, etc.) can be "summed" by using the retention time of the compounds on some standard gas chromatographic column. Such experiments have been performed on the compounds you present (multi-ring aromatics, poly-chlorinated species, etc.). I think use of these laboratory data will help you assign better (relative) values to your assumed values of Henry's Law Constant, Molecular Diffusivity and Reactivity, particularly if chromatograms are run at multiple temperatures. As you pointed out, uncertainties in the fraction sorbed on particles predominate in your approach. The above experiments measure sorption directly, provided an acceptable stationary phase is selected.

W. J. LYMAN: Dr. Delumyea is correct in pointing out that several environ-mentally-important properties of organic chemicals can be determined by the measurement of the retention time on calibrated chromatographic columns. In-cluded, for example, are octanol-water partition coefficient, water solubility, soil adsorption coefficient and vapor pressure. Such determination methods are of great interest because of their simplicity and rapidity. We point out, however, that one objective of our paper is to investigate the possibility of estimating certain properties from structural information only, i.e., without recourse to laboratory measurements. Whenever time and budget allow, measured values should always be obtained and used in studies of this nature. Our paper (and other works cited therein) shows that reasonable preliminary assessments can often be made using--if necessary--property estimates based on structure alone.